Acid buffer action: The weak acid, HA, transfers protons to OH\(^{-}\) ions supplied by strong base. The conjugate base, A\(^{-}\), of the weak acid accepts protons from the H\(_3\)O\(^{+}\) ions supplied by a strong acid.

A strong acid and the salt of its conjugate base don't make a good buffer. Why?

Base Buffer Example: \(\text{NH}_3\) (aq) + H\(_2\)O (l) \(\iff\) \(\text{NH}_4^+\) (aq) + OH\(^{-}\) (aq)

When strong acid is added, \(\text{NH}_3\) accepts protons from incoming acid to make \(\text{NH}_4^+\). When strong base is added, \(\text{NH}_4^+\) donates a proton to form \(\text{NH}_3\) and H\(_2\)O. pH remains the same.

Base buffer action: The weak base, B, accepts protons supplied by strong acid. The conjugate acid, BH\(^{+}\), of the weak base transfers protons to the OH\(^{-}\) ions supplied by a strong base.

A buffer is a mixture of weak conjugate acids and bases that stabilize the pH of a solution by providing a source or sink for protons.

Sample Buffer Problem: Suppose 1.00 mol of HCOOH and 0.500 mol of NaHCOO are added to water and diluted to 1.0 L. Calculate the pH. \(K_a = 1.77 \times 10^{-4}\)

\[
\begin{array}{ccc}
\text{initial molarity} & \text{HCOOH} & \text{H}_2\text{O} & \text{HCOO}^- \\
1.00 & 0 & 0.500 \\
\text{change in molarity} & -x & +x & +x \\
\text{equilibrium molarity} & 1.00 -x & +x & 0.500 + x \\
\end{array}
\]

\(K_a = 1.77 \times 10^{-4}\) =

Using approximation that x is small compared to 1.00 and 0.500, x=

Check assumption

pH =

Now - what if 0.100 mol of a strong acid (HCl) had been included in the 1.0 L solution. Because 0.100 mol of HCl reacts with equal number of moles of HCOO\(^{-}\) to form equal moles of HCOOH:

For HCOO\(^{-}\), 0.500 mol - 0.100 mol = 0.400 mol \quad [\text{HCOO}^-] = 0.400 \text{ mol/1.0 L} = 0.400 \text{ M}
For HCOOH, 1.00 mol + 0.100 mol = 1.10 mol \quad [\text{HCOOH}] = 1.10 \text{ mol/1.0 L} = 1.10 \text{ M}
HCOOH + H₂O ⇌ H₃O⁺ + HCOO⁻

Kₐ = 1.77 x 10⁻⁴

Using approximation that x is small compared to 1.10 and 0.40, x=

Check assumption (5% rule)

pH = 3.31

So addition of 0.10 mol of strong acid only changed pH from 3.45 to 3.31

Designing a Buffer

One must consider the relationship between the ratio of [HA] to [A⁻], the pKₐ, and the desired pH.

HA (aq) + H₂O ⇌ H₃O⁺ (aq) + A⁻ (aq)  \[ K_a = \frac{[H_3O^+] [A^-]}{[HA]} \]

Rearrange: \[ [H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \]

Take logarithms of both sides: \[ \log [H_3O^+] = \log K_a + \log \frac{[HA]}{[A^-]} \]

Multiply by (-): \[ -\log [H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \]

That is: \[ pH = pK_a - \log \left( \frac{[HA]}{[A^-]} \right)_{eq} \]

The values of [HA] and [A⁻] in the equation are at equilibrium. However, a weak acid HA typically loses only a tiny fraction of its protons, so [HA] is negligibly different from the molarity of the acid.
used to prepare the buffer. Likewise, only a tiny fraction of the weakly basic anions of $A^-$ accept protons, so $[A^-]$ is negligibly different from the molarity of $A^-$ used to prepare the buffer.

\[
\text{So } \quad \text{pH } \approx \text{pK}_a - \log \left( \frac{[HA]}{[A^-]} \right) \quad \text{Henderson-Hasselbalch Equation}
\]

This assumption is valid when $[H_3O^+]$ is small compared to $[HA]$ and $[A^-]$ (i.e. less than 5%).

**Example: Design a buffer system with pH 4.60.**

A buffer solution is most effective in the range of $\text{pK}_a \pm 1$

Acetic acid is suitable with a $\text{pK}_a$ of 4.75

\[
\begin{align*}
\text{pH} &= \text{pK}_a - \log \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right) \\
\text{log} \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right) &= \text{pK}_a - \text{pH} = 4.75 - 4.60 = 0.15 \\
\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} &= 10^{0.15} = 1.4
\end{align*}
\]

The ratio is more important than the amounts used. However, the amounts used do affect the capacity of the buffer to resist changes in pH. Higher concentrations = more resistance to change.

If you use too low concentrations, the Henderson-Hasselbalch equation won’t be valid.

For pH 4.60, $[H_3O^+]$ is $2.5 \times 10^{-5}$.

\[
2.5 \times 10^{-5} \times 100\% < 5\%
\]

$[HA]$ or $[A^-]$ need to be $> 5.0 \times 10^{-4}$ M

---

**Today’s material**

**Acid Base Titrations**

An acid-base titration is the addition of a volume of base of known concentration to acid of unknown concentration (or addition of acid to base). This technique can be used to determine the concentration of an acid or base.

**Titrations involving a strong acid and a strong base**

In a titration of a strong acid with a strong base, or a strong base with a strong acid, the pH changes slowly initially, changes rapidly through pH 7 at the equivalence point and then changes slowly again.
Titration curves:

Equivalence (stoichiometric, S) point = the theoretical volume at which the amount of base added equals the amount of acid that was originally present.

End point = the experimentally measured volume at which the indicator changes color.

Endpoint should equal equivalence point.

Calculating points on a pH curve.
Example: a strong base (0.250 M NaOH) is titrated with a strong acid (0.340 M HCl)

1. Calculating the pH before the equivalence point when 5.00 mL of 0.340 M HCl (aq) is added to 25.00 mL of 0.250 M NaOH (aq)

A). Calculate moles of OH\(^-\) present. (Base is strong so amount of NaOH added = amount of OH\(^-\) formed.)

\[
0.02500 \text{ L} \times 0.250 \text{ mol/L} = 6.25 \times 10^{-3} \text{ moles}
\]

B). Calculate moles of H\(_3\)O\(^+\) supplied by titrant. (Acid is strong so HCl added = H\(_3\)O\(^+\) formed.)

\[
0.00500 \text{ L} \times 0.340 \text{ mol/L} = 1.70 \times 10^{-3} \text{ moles}
\]

C). Find the moles of OH\(^-\) remaining after the reaction with H\(_3\)O\(^+\) ions.

because stoichiometry is 1:1

\[
6.25 \times 10^{-3} \text{ moles} - 1.70 \times 10^{-3} \text{ moles} = 4.55 \times 10^{-3} \text{ mol of OH}^- \text{ left}
\]

D). Calculate molarity of OH\(^-\)

\[
4.55 \times 10^{-3} \text{ mol/0.03000 L} = 0.152 \text{ mol/L (Make sure to use total volume 5.00 mL + 25.00 mL)}
\]

E). Calculate pH

\[
pOH = -\log 0.152 = 0.818 \quad pH = 14.00 - 0.818 = 13.18
\]
2. Calculating the volume of HCl needed to reach the equivalence point.

Initially 6.25 x 10^{-3} mol of OH were present. At the equivalence point, 6.25 x 10^{-3} mol of HCl will have been added (1:1 stoichiometry)

\[
6.25 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.340 \text{ mol}} = 0.0184 \text{ L}
\]

What is the pH at the equivalence point?

3. Calculate the pH after 1.00 mL of HCl has been added after equivalence point has been reached.

A). Find moles of H_3O^+ formed due to the 1.00 mL addition of HCl

\[\text{H}_3\text{O}^+ \text{ formed} = \text{amount of HCl added, since strong acid}\]

\[0.340 \text{ mol/L} \times (0.00100 \text{ L}) = 3.40 \times 10^{-4} \text{ mol of H}_3\text{O}^+\]

B). Calculate molarity of H_3O^+

C). pH = -\log (7.66 \times 10^{-3}) = 2.116

**Titration Curves for Weak acid/Strong base and for Weak base/Strong acid**

![Titration Curves](https://openocw.mit.edu)
Example: Titration of weak acid with strong base
25.0 mL of 0.10 M HCOOH with 0.15 M NaOH (K_a = 1.77 x 10^{-4} for HCOOH)

1. Volume = 0 mL of NaOH added
Before any NaOH is added, the problem is that of an ionization of a weak acid in water.

\[
\text{HCOOH (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{(aq) + HCO}_2^- \text{(aq)}
\]

\[
\begin{array}{c|c|c|c}
\text{initial molarity} & \text{HCOOH (aq)} & \text{H}_3\text{O}^+ \text{(aq)} & \text{HCO}_2^- \text{(aq)} \\
\text{change in molarity} & -x & +x & +x \\
\text{equilibrium molarity} & 0.10-x & x & x
\end{array}
\]

\[
K_a = 1.77 \times 10^{-4} = (x)^2/(0.10-x) = (x)^2/0.10
\]

\[
x = 0.00421 \text{ (check 0.00421 is 4.2% of 0.10) okay}
\]

\[
\text{pH} = -\log [0.00421] = 2.38 \text{ (to how many sig figs?)}
\]

2. \(0 < V < V_{eq}\)
In this range, the acid has been partly ionized by the strong base (buffering region).

Calculate the pH of the solution resulting from the addition of 5.0 mL of 0.15 M NaOH. Because OH^- is a stronger base than HCO_2^-, it reacts almost completely with HCOOH.

\[
\text{HCOOH (aq) + OH}^- \text{(aq) } \rightarrow \text{H}_2\text{O (l) + HCO}_2^- \text{(aq)} \quad K>>1
\]
Initial Moles
For HCOOH, \((25.0 \times 10^{-3} \text{ L})(0.10\text{M}) = 2.5 \times 10^{-3}\) moles
For OH\(^-\), \((5.0 \times 10^{-3} \text{ L})(0.15\text{M}) = 0.75 \times 10^{-3}\) moles

Moles after Reaction
\(2.5 \times 10^{-3}\) moles - 0.75 \(\times 10^{-3}\) moles = 1.75 \(\times 10^{-3}\) moles of HCOOH left
0.75 \(\times 10^{-3}\) moles OH\(^-\) produces 0.75 \(\times 10^{-3}\) moles of HCO\(_2^\text{⁻}\)

Molarity
1.75 \(\times 10^{-3}\) moles of HCOOH/ (0.0250 + 0.0050 L) = 0.0583 M HCOOH
0.75 \(\times 10^{-3}\) moles of HCO\(_2^\text{⁻}\) / (0.0250 + 0.0050 L) = 0.0250 M HCO\(_2^\text{⁻}\)

Option 1

<table>
<thead>
<tr>
<th></th>
<th>HCOOH</th>
<th>(\text{H}_2\text{O}^+ + \text{HCO}_2^\text{⁻})</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial molarity</td>
<td>0.0583</td>
<td>0</td>
</tr>
<tr>
<td>change in molarity</td>
<td>-x</td>
<td>+x +x</td>
</tr>
<tr>
<td>equilibrium molarity</td>
<td>0.0583 -x</td>
<td>+x</td>
</tr>
</tbody>
</table>

\[K_a = 1.77 \times 10^{-4} = \frac{(0.0250 + x)(x)}{(0.0583-x)}\]
assume \(x\) is small \(\approx\) \(\frac{0.0250x}{0.0583-x}\)
\(x = 4.13 \times 10^{-4}\)
Check assumption: 4.13 \(\times 10^{-4}\) is 1.65\% of 0.025 and is 0.7\% of 0.0583 okay
\[\text{pH} = -\log [4.13 \times 10^{-4}] = 3.38\]

Option 2

\[\text{pH} \approx pK_a - \log ([\text{HA}]/[\text{A}^-])\]
\[\text{pH} \approx 3.75 - \log ([0.0583]/[0.0250]) = 3.75 - 0.368 = 3.38\]
check assumption: for a pH of 3.38, [\(\text{H}_3\text{O}^+\)] = 4.2 \(\times 10^{-4}\) and that is <5\% of 0.0583 and is <5\% of 0.0250. Okay

If the 5\% assumption is not valid, than option 1 must be used and
\[K_a = 1.77 \times 10^{-4} = \frac{(0.0250 + x)(x)}{(0.0583 - x)}\] can not be simplified.
Must solve by quadratic equation.

Note: when the volume of NaOH added is between 0 and the equivalence volume \(V_{eq}\), the problems are similar to buffer problems. This region of the titration curve is called the "buffering region."
**Half-equivalence point**

When the volume of NaOH added is equal to half the equivalence volume, \([HA] = [A^-]\).

\[
pH \approx pK_a - \log ([HA]/[A^-])
\]

\[
pH \approx pK_a - \log (1)
\]

\[
pH \approx pK_a
\]

3. \[ V = V_{eq} \]

At the equivalence point, the amount of NaOH added is equal to the amount of HCOOH. The pH is not 7 as it is for a strong acid and a strong base. The pH is >7 when a weak acid is titrated with a strong base. The pH depends on the properties of the salt formed during the neutralization process. HCOOH and NaOH form NaHCO\(_2\) and H\(_2\)O. Na\(^+\) has no effect on pH and HCO\(_2\)\(^-\) is a base. Thus at the equivalence point, the pH is >7.

**Calculate the pH at the equivalence point**

**Calculate total volume at equivalence point**

moles of HCOOH = 2.5 \times 10^{-3} \text{ moles} = \text{ moles of HCO}_2^- \text{ formed} = \text{ moles of OH}^- \text{ added}

\[
2.5 \times 10^{-3} \text{ moles of OH}^- \times \frac{\text{L}}{0.15 \text{ mol}} = 1.67 \times 10^{-2} \text{ L of NaOH added}
\]

Total volume = 0.0250 L + 0.0167 L = 0.0417 L

**Molarity of HCO\(_2\)^-**

2.5 \times 10^{-3} \text{ moles of HCO}_2^- / (0.0417 L) = 0.0600 M HCO\(_2\)^-

This is an ionization of weak base in water problem.

\[
\text{HCO}_2^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HCOOH} (aq) + \text{OH}^- (aq)
\]

<table>
<thead>
<tr>
<th>(\text{HCO}_2^- (aq))</th>
<th>(\text{HCOOH} (aq))</th>
<th>(\text{OH}^- (aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{initial molarity}</td>
<td>0.0600</td>
<td>0</td>
</tr>
<tr>
<td>\text{change in molarity}</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>\text{equilibrium molarity}</td>
<td>0.0600-x</td>
<td>+x</td>
</tr>
</tbody>
</table>

You can take it from here. Simplify if x is small compared to 0.0600 M. Calculate x, which is equal to [OH\(^-\)] = 1.83 \times 10^{-6} M. Then calculate pOH = 5.74. From pOH, calculate pH.

pH = 8.26 (which is >7)
Beyond the equivalence point, NaOH is added to the solution of the conj. base HCO$_3^-$.

Since \( \text{HCO}_3^- \) does not give rise to much \( \text{OH}^- \) in solution \( (1.83 \times 10^{-4} \text{ M}) \), the pOH and pH are determined by the amount of excess NaOH added. This problem is similar to a strong acid/strong base problem.

At 5.00 mL past the equivalence point:

\[
0.00500 \text{ L} \times 0.15 \text{ M} = 7.5 \times 10^{-4} \text{ moles excess OH}^-
\]

\[
7.5 \times 10^{-4} \text{ moles OH}^- / (0.00500 \text{ L} + 0.0250 \text{ L} + 0.0167 \text{ L}) = 0.016 \text{ M OH}^-
\]

pOH = \(-\log [0.16] = 1.79\)

pH = 12.21